

1 Apparatus and Technique for Measuring Permeability
2 and Permeant Sorption

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5 Cross-Reference to Related Applications

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8 This application claims the benefit of U.S. Provisional
9 Application Number 60/418,444, filed 15 October 2002.

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12 Field of the Invention

13
14 The invention relates to measuring material permeability
15 characteristics.

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17 More specifically, it relates to measuring gas or vapor
18 diffusion through packaging materials.

19
20 Even more specifically, it relates to measuring the flux
21 of CO₂ through bottles and films such as those used for
22 packaging carbonated beverages.

Background of the Invention

Plastics materials are increasingly being used in packaging applications, replacing glass and metal. However, plastic materials generally have inferior vapor barrier properties compared to glass and metal containers. Accordingly, plastic packages generally admit oxygen into the package at a faster rate, show higher aroma loss, higher water vapor loss, and greater CO₂ loss in case of carbonated beverage packages. Other advantages afforded by plastics such as lighter weight, lower cost, the ability to form attractive container shapes continues to sustain or increase the share of plastics in packaging applications. Improved test methods are therefore constantly being developed to measure plastics barrier properties.

When the permeant of interest is CO₂, for example, in measuring shelf life of carbonated beverage packages, two broad categories of methods are presently used. The first methods measure retained CO₂ in the packages by periodically measuring CO₂ in a simulated shelf-life test. The second methods measure the rate of CO₂ loss from the package at a point in time and at a measured driving force (partial pressure) in the container. For typical packages of interest, methods measuring retained CO₂ have several deficiencies. The CO₂ content changes only

1 very slightly (10 to 15%) during the shelf life, demanding
2 exquisite sensitivity in the detection mechanism because one is
3 required to measure such small changes over a large offset. In
4 addition, such small signal changes occur over very long
5 periods of time (8 to 12 weeks - essentially the expected shelf
6 life of the package) rendering these methods useless for rapid
7 permeation assessment. As such, these methods are of little
8 predictive value. The CO₂ loss rate measurement methods, which
9 in principle can measure the signal without having to measure
10 against a large offset as in the retained CO₂ methods, in their
11 current implementation have several disadvantages as discussed
12 below. Although loss rate methods are faster than the retained
13 CO₂ methods, they are often inaccurate and shelf life
14 predictions from such methods often do not concur with
15 measurements using the retained CO₂ tests. The present
16 invention overcomes deficiencies of the loss rate measurement
17 methods in prior art and thus provides a method that is not
18 only very rapid, but also predicts shelf life with accuracy.

19

20 Several techniques and apparatus for measuring oxygen
21 permeability of plastic films are patented and published.
22 Usually, the film sample of interest is sandwiched between two
23 test chambers using appropriate sealing mechanisms. One
24 chamber is exposed to the permeant gas of interest in high
25 concentrations while the second chamber is purged continuously

1 with an inert carrier gas. Any permeated permeant from the
2 first chamber is thus transported to a permeant detector
3 located outside these permeation chambers. The detector itself
4 is usually a sensor that is capable of measuring extremely
5 small concentrations of the permeant. While in principle the
6 method can also be applied to testing containers, such a
7 configuration does not lend itself to nondestructive testing of
8 whole containers.

9

10 Use of such a continuous purging system is also
11 disadvantageous for other reasons. The concentration of
12 permeated permeant is often extremely small in the second
13 chamber, especially when the sample material is a good barrier.
14 Measuring such low concentrations of the permeants reliably is
15 a challenge for most sensors. Furthermore, such low permeant
16 concentrations are diluted several fold when a carrier gas is
17 used to transport the permeated permeant to the remote
18 detector. The objective of the measurement, the true
19 permeation rate is directly related to the product of carrier
20 gas flow rate and the detector response. For accurate
21 estimation of permeation rates, it becomes essential that the
22 flow rate of the carrier gas be accurately and robustly
23 controlled, and also that the detector be capable of exquisite
24 sensitivity.

25

1 In addition, the permeability of many barrier materials is
2 highly sensitive to temperature and humidity conditions at the
3 time of the test. For example, CO₂ permeability of EVAL-F, a
4 commercially available barrier material, increases about 30-
5 fold when the relative humidity increases from 50% to 90%.
6 Most beverage packages contain 100% relative humidity inside
7 the package. It is of interest to measure permeability under
8 precisely defined high external humidity conditions. To my
9 knowledge, the relevant prior art does not teach how testing at
10 precisely controlled high relative humidities is to be
11 conducted. Precise control of humidity, especially at high
12 humidity levels is difficult to achieve in current systems
13 mainly because of the difficulty associated with controlling
14 humidity in a continuous purge stream. Further, humidity
15 control in the first chamber, where the permeant source is
16 provided is even more difficult, and is left uncontrolled.

17
18 An example of non-flowing systems used for package
19 permeability testing is described in US patent application
20 US20020194899A1 published December 26, 2002, titled "Method and
21 Device for the Determination of the Gas Permeability of a
22 Container" (equivalent world patent WO 0148452). Here,
23 packages containing high partial pressures of the permeant are
24 placed in a confinement chamber in such a way as to minimize
25 the spacing between the package and the chamber. As the

1 permeant permeates to this inter-space, the pressure therein
2 increases and is measured with a sensitive pressure gage. The
3 disadvantage with such a system is that plastic containers
4 expand under pressure. Thus, the volume of the inter-space can
5 change significantly causing erroneous pressure readings.
6 Thus, while this method could be faster than the retained CO₂
7 methods, its practical utility is limited to measuring relative
8 barrier property differences between different packages rather
9 than absolute permeability measurements for each package
10 independently that is necessary for shelf life predictions.
11 Further, since the method relies heavily on minimizing the
12 volume of the inter-space between the given confining chamber
13 and the package, significant deviations in the test package
14 shape or size will require completely different chambers to be
15 used. Lastly, methods for accurate humidity control that are
16 critical for most barrier property testing are not taught in
17 the above described US patent application.

18

19 Another example of a non-flowing system used in the field
20 of vacuum insulation panel testing is described in US patent
21 5,345,814, issued 13 September 1994, and entitled "Method and
22 Apparatus for Testing Vacuum Insulation Panel Quality". Vacuum
23 insulation panels are prepared by evacuating air and
24 introducing small quantities of helium tracer gas into the
25 panels just prior to sealing. The panels are placed in an

1 evacuated chamber at an even lower pressure than within the
2 panels and the helium is allowed to flow out of the insulation
3 panel into the chamber space. The integrity of the panels is
4 assessed by sampling the chamber gases to measure the rate of
5 helium accumulation. While this approach overcomes some of the
6 limitations of the continuous purge systems, it uses a flow or
7 a sniffer type detector, and relies on the contents of the
8 chamber to be exhausted with an elaborate equipment set up.
9 Most critically, the '814 patent does not teach ways of
10 temperature and humidity control in package testing.

11

12 Further, no prior art references teach a method for
13 measuring sorption of the permeant by the packaging materials
14 empirically.

15

16 It would be highly advantageous, therefore, to remedy the
17 foregoing and other deficiencies inherent in the prior art.

18

19 Accordingly, it is an object of the present invention to
20 provide new and improved apparatus and techniques for measuring
21 package permeability.

22

23 Another object of the invention is to provide new and
24 improved apparatus and techniques for measuring package
25 permeant sorption.

1 Another object of the invention is to provide new and
2 improved package permeability measuring apparatus and
3 techniques that are extremely accurate.

4

5 Another object of the invention is to provide new and
6 improved package permeability measuring apparatus and
7 techniques that are substantially faster than prior art
8 apparatus and techniques.

9

10 A further object of the invention is to provide new and
11 improved package permeability measuring apparatus and
12 techniques that can be used on substantially any types, shapes,
13 and sizes of packages.

14

15 A further object of the invention is to provide new and
16 improved apparatus and techniques for measuring package
17 permeant sorption wherein accurate control of humidity and
18 temperature are better achieved.

Summary of the Invention

Briefly, to achieve the desired objects of the instant invention in accordance with a preferred embodiment thereof, apparatus and methods for measuring package permeability and/or permeant sorption are disclosed. The apparatus includes a housing defining a sealed chamber that is substantially impervious to the permeant of interest. The chamber has an inlet for introducing an inert medium substantially free of the permeant and an outlet for removing the inert medium. A sensor is positioned within the chamber to provide signals indicative of permeant concentrations within the chamber. A sealable opening is provided in the housing so that packages, to be measured for permeability and/or permeant sorption, can be introduced within the chamber. In the method, testing of permeant concentrations is cycled to determine the slope of a time line between a low and a high concentration of the permeant. Humidity and temperature are preferably maintained constant within the chamber during testing.

Accurate and precise humidity controlling apparatus is also disclosed. The humidity controlling apparatus includes a bag or package formed of microporous hydrophobic material, such as GORTEXTM, or Celgard 2500TM. The bag or package contains a saturated salt solution together with some excess undissolved

1 salt specifically selected to maintain a desired humidity
2 within the chamber. The size of the bag and the amount and
3 type of salt solution contained therein is pre-calculated to
4 maintain the selected humidity in the chamber or other closed
5 area.

Brief Description of the Drawings

The foregoing and further and more specific objects and advantages of the instant invention will become readily apparent to those skilled in the art from the following detailed description of a preferred embodiment thereof taken in conjunction with the drawings, in which:

FIG. 1 is a semi-schematic diagram illustrating testing apparatus and a method of apparatus set-up in accordance with the present invention;

FIG. 2 is a graphical representation of an acquired signal in the apparatus set-up of FIG. 1, which acquired signal is further analyzed as described in the specification;

FIG. 3 is a simplified sectional view of a test package for measuring permeabilities of films in accordance with the present invention;

FIG. 4 is a semi-schematic diagram illustrating optional agitation, temperature and relative humidity control apparatus, in accordance with the present invention;

1 FIG. 5 illustrates a graphical representation of the
2 results of a method performed in accordance with the present
3 invention; and

4

5 FIG. 6 is a plot of permeant desorbed and calculated as
6 the product of the sensed concentration and the test chamber
7 volume in a method performed in accordance with the present
8 invention.

Detailed Description of the Preferred Embodiments

Turning now to the drawings in which like reference characters indicate corresponding elements, attention is first directed to FIG. 1 which illustrates a housing 9 defining an inner sealed chamber 10 with several attachments. Housing 9 and all the attachments are preferably made of materials substantially impervious to the permeant of interest, for example, stainless steel. Tubings 11 and 12, connected to an inlet and an outlet, respectively, of chamber 10, are used to flush chamber 10 with an inert medium. A valve 19 connected to tubing 11 and a valve 20 connected to tubing 12 are included for this purpose. A permeant sensor 13 is conveniently located at least partially within chamber 10 so that permeant within chamber 10 can be sensed and noted externally of chamber 10. The inert medium, which is also substantially free of the permeant, is chosen such that it does not interfere with the detection of permeant by permeant sensor 13.

For example, if carbon dioxide (CO₂) is the permeant of interest, one could use nitrogen or air substantially free of CO₂ as the inert medium. Permeant sensor 13 is ideally located within the chamber to measure the changes in permeant concentration directly, as opposed to embodiments where a carrier gas transports the contents of chamber 10 to a sensor

1 placed separate from chamber 10 but connected to chamber 10 by
2 appropriate plumbing. Permeant sensor 13 is ideally based on
3 the well known method of infrared radiation absorption for the
4 permeants that significantly absorb at specific wavelengths in
5 the infrared spectrum of electromagnetic radiation. However,
6 any sensitive method of permeant quantification can be suitably
7 chosen as applicable for the permeant of interest.

8
9 Chamber 10 has an opening 14 through which test samples,
10 for example test samples 17 and 18, are introduced. A sealing
11 cover 15 is removably connected over opening 14 and is sealed
12 against opening 14 by an O-ring or a gasket type seal 16. Seal
13 16 is preferably made of formulations that exhibit low
14 permeability for the permeant in question, for example, high-
15 barrier elastomers and metallic seals. Following introduction
16 of test samples 17 and 18 into chamber 10, opening 14 is closed
17 and sealed by cover 15. Although only two test samples are
18 depicted, it should be realized that any suitable number of
19 samples that the container could accommodate could be used.
20 Indeed, it is preferable to use as many test samples or
21 packages as possible to shorten the test time. In this
22 specific example, test samples 17 and 18 are bottles with
23 appropriate closures, but any other choice of test samples or
24 packages, filled with any substance that contains or generates
25 a permeant of interest, can be tested.

1 The following example describes the application for
2 measuring CO₂ permeation rates through plastic bottles, and
3 sorption of CO₂ by such packaging materials. The plastic
4 bottles, in this example test samples 17 and 18, are filled
5 with a carbonated beverage or carbonated water at a known
6 carbonation level, or simply with CO₂. The latter is
7 conveniently achieved by weighing out appropriate amounts of
8 dry ice and capping the bottle. Carbonated water could be
9 prepared in the bottle by adding appropriate amounts of a
10 carbonate or bicarbonate salt to a bottle filled with an
11 aqueous medium, and adding a second reagent to decrease the pH
12 of the medium below pH 5, most preferably, below pH 4.5 to
13 insure liberation of substantially all the CO₂ from the
14 bicarbonate. Alternately, a large batch of carbonated water
15 could be simply filled into the packages using any filling
16 device. If the carbonation level is not known prior to the
17 start of the permeation test, it could also be determined by a
18 suitable method after the test.

19

20 Test samples 17 and 18 are attemperated to the desired
21 temperature at which the permeability is to be measured,
22 preferably prior to introducing them into chamber 10. Most
23 preferably, test samples 17 and 18 are prepared at the
24 appropriate test temperature so no special attemperation step
25 is required.

1 Once test samples 17 and 18 are introduced into chamber 10
2 and opening 14 is closed and sealed, valves 19 and 20 are
3 opened, and chamber 10 is flushed, if necessary, with a
4 suitable inert medium, for example, air. The inert medium is
5 supplied to chamber 10 through valve 19 and tubing 11 while
6 chamber 10 is vented through tubing 12 and valve 20. The
7 volume of the inert medium used should be adequate to reduce
8 the permeant concentration to suitably low levels, for example
9 below the sensitivity (lowest accurately measurable permeant
10 concentration) of permeant sensor 13. The inert medium could
11 be appropriately preconditioned for the desired test
12 conditions, for example temperature and relative humidity,
13 before its entry into chamber 10. Following such a chamber
14 flush, valves 19 and 20 are closed to completely isolate
15 chamber 10 from the outside environment. CO₂ emitted by test
16 samples 17 and 18 accumulates in chamber 10 and such increase
17 in CO₂ concentration is measured by permeant sensor 13. In
18 this preferred embodiment, signals from sensor 13 are recorded,
19 externally, with a suitable device 13A to generate a history of
20 permeant concentration over time.

21

22 Attention is next drawn to FIG. 2, which is a graphical
23 representation of typical permeant concentration history during
24 a test in accordance with the present invention. If the
25 package materials are relatively free of CO₂ (or the permeant

1 in question) prior to packaging test samples 17 and 18 with
2 carbonated substances, in this example, then steady state
3 permeation is not established immediately in such packages.
4 The rate of permeation through the packages and thus permeant
5 accumulation rate in chamber 10 increases with time until a
6 steady state is established whence it attains a substantially
7 constant value. During the period of increasing permeation
8 rates, shown as curve 23, the packaging materials absorb the
9 permeant until they substantially saturate. Such a process of
10 saturation is called henceforth "sorption" or "adsorption".
11 Typically, it takes about 1 to 7 days for the sorption process
12 to substantially complete. Until the sorption process is
13 substantially complete, the permeation rate does not reach the
14 steady state constant value. When the packages have been
15 packaged significantly ahead of time, then such changes in
16 permeation rates may not be readily apparent because permeation
17 may have already substantially stabilized to the steady state
18 permeation conditions. It must be noted that such time-
19 dependent permeation rates are also seen whenever the test
20 conditions (such as temperature, or humidity, or any other
21 relevant test parameter) represent a deviation from those at
22 which the package was equilibrated to prior to the test.

23

24 When the permeant concentration in chamber 10 increases to
25 a suitably set high limit, designated 22 in FIG. 2, valves 19

1 and 20 are opened and chamber 10 is rapidly flushed with enough
2 volume of the inert medium so as to reduce the permeant
3 concentrations below a suitable low limit, designated 21 in
4 FIG. 2. Suitable high limits are chosen such that the partial
5 pressure of the permeant in chamber 10 is still substantially
6 lower than that inside test samples 17 and 18 so that the
7 accumulation of the permeant in chamber 10 would not
8 significantly alter the permeation rate. Once low limit 21 is
9 crossed, the inert medium flush is stopped, and valves 19 and
10 20 are closed to isolate chamber 10 and initiate another round
11 of measurements.

12

13 Sensor signals can be continuously acquired through these
14 recycling steps until the test procedure is stopped. The
15 signal collected appears similar to that depicted in FIG. 2,
16 where each cycle of chamber flush quickly decreases the chamber
17 permeant concentration to low limit 21. While the first
18 permeation cycle, e.g., 23, may show increasing permeation
19 rates and nonlinear behavior, the monitoring of subsequent
20 permeation steps produces progressively more linear
21 accumulation profiles as shown in cycles 24, 25, and 26. Note
22 that in FIG. 2, substantial nonlinear permeation is shown only
23 in the first measurement cycle, it is possible to see
24 significant nonlinearities in several of the subsequent
25 measurement cycles depending on the actual test samples and the

1 test conditions employed. The slope of each line segment in
2 FIG. 2 increases gradually with each new cycle until steady
3 state permeation is achieved when such slopes will remain
4 substantially constant between successive cycles.

5
6 Instead of acquiring the sensor signal continuously, one
7 may simply record the time intervals for the signal to reach
8 the high limit from the low limit and thus calculate the rate
9 of permeation into the chamber space. However, the slope of
10 the sensor signal lines is better calculated by a linear
11 regression of the collected sensor signal vs. time data because
12 it allows for early estimation of the permeation rates without
13 necessarily waiting till the concentration reaches the high
14 limit setting. Further, it is advantageous to acquire the
15 signal continuously when nonlinear behavior is to be analyzed,
16 for example, when the objective is to determine the amount of
17 CO₂ that the package adsorbs from a beverage. This application
18 will be discussed later in this specification.

19
20 From the slopes of the sensor signal vs. time history (s)
21 for each measurement cycle, one can calculate the rate of
22 permeant loss R from each package by considering the total
23 available chamber volume (V_{ch}), the total number of packages
24 (N_{pkg}) (test samples 17, 18, etc.) placed in chamber 10, and the
25 volume displaced by each package (V_{pkg}) thus:

$$R = \frac{s(V_{ch} - N_{pkg} V_{pkg})}{N_{pkg}} \quad (\text{eq. 1})$$

2

3 The packages should be identically prepared such that each
 4 package is substantially the same as the rest in its initial
 5 permeant charge (driving force). The steady state permeation
 6 rate can be calculated by averaging the rates measured for
 7 several cycles after the steady state is achieved. Whether the
 8 steady state is attained could be determined by appropriate
 9 statistical test methods such as analysis of variance (ANOVA)
 10 and ensuring that an adequate number of measurement cycles are
 11 run to achieve the desired confidence level. Finally, average
 12 package permeability (P) is estimated by dividing the observed
 13 permeation rate (R) by the driving force partial pressure (p)
 14 or the permeant in the containers:

15

$$P = \frac{R}{p} \quad (\text{eq. 2})$$

17

18 If the total amount of permeant in the packages is known
 19 at the beginning of the test, then one can estimate the time it
 20 takes for the loss of a fixed percentage of the permeant to
 21 occur. When measuring CO₂ loss from packages, typically the
 22 test can be completed in several minutes to several days
 23 depending on the barrier properties of the packaging materials

and the history of the packages prior to the start of the test. Based on any arbitrary percentage loss tolerance specification (L) from an initial permeant charge (C^0), it is thus possible to predict accurately the retained permeant amounts at different times ($C(t)$) or shelf life (t) of the packaged product for several weeks or months hence using the following formulas:

$$C(t) = C^0 \cdot e^{-\left(\frac{PH}{V_L + \phi V_H}\right)t} \quad (\text{eq. 3})$$

and

$$t = -\left(\frac{V_L + \phi V_H}{PH}\right) \cdot \ln(1 - L) \quad (\text{eq. 4})$$

where P is the permeability of the package (cc/pkg/d/atm), H is the solubility of the gaseous permeant in the liquid contained in the package (cc/atm), V_L and V_H are the volumes of liquid and headspace in the package (cc). ϕ is a correction factor to account for the fact that the headspace of the container is also a source for the permeant and is defined thus:

$$\phi = \frac{HT^*}{p^*T} \quad (\text{eq. 5})$$

1 where T is the test temperature, and p^* and T^* are the
2 pressure and temperature at which the volumes of permeant are
3 referenced.

4
5 The advantages of the present invention will become
6 evident upon examining FIG. 5. The subject packages of this
7 graph were plastic barrier bottles packaged with carbonated
8 water at conditions that allow packaging substantially free of
9 air. They were then preconditioning at 75°F and 75% relative
10 humidity for 1 week in an environmental chamber to allow for
11 bottle expansion under pressure ("creep") and CO₂ sorption to
12 substantially complete and attain a steady state permeation
13 regime. Although only 8 bottles were used for the permeation
14 testing based on the current invention, many more were packaged
15 in order to run a traditional long-term shelf life test for
16 retained CO₂. The art of temperature and humidity control used
17 here is disclosed later in this patent application.

18
19 Following 1 week of such preconditioning, 8 bottles were
20 placed in the test chamber of the subject invention and the
21 rate of CO₂ accumulation was measured with an infrared
22 absorption sensor that is placed within the chamber. Room air
23 was used as the inert medium and a set of 6 measurement cycles
24 were conducted as described over a 3-day period. The driving
25 force partial pressure of CO₂ in the packages was measured by

1 measuring the pressure in each of the 8 packages tested and
2 averaging over the eight measurements. Using equation (3)
3 above, the retained CO₂ was thus estimated using the known
4 driving force values as the initial permeant charge (C⁰). The
5 solid line of FIG. 5 represents charting of equation 3. The
6 traditional long-term shelf life test was also conducted by
7 periodically removing 3 to 5 bottles from the environmental
8 chamber at different points into the shelf life for several
9 months to measure retained CO₂ levels. The CO₂ content in the
10 packages was measured by measuring pressure in the bottles
11 using a piercing device (thus a destructive test). Average CO₂
12 content, together with error bars representing standard
13 deviations for each measurement point are also plotted as
14 symbols on FIG. 5.

15

16 It can be seen that the current method produces results
17 that are in excellent agreement with the conventional shelf-
18 life test that lasted over 6 months. Not only is the present
19 test method of predictive value, it is also extremely rapid (3
20 days compared to 6 months for the traditional method).
21 Further, since the test period is generally very short compared
22 to typical package shelf life, the package loses only a
23 negligible amount of the permeant, and thus the test can be
24 considered nondestructive.

1 It must be noted that room air was used in this test
2 method as a purge gas to clear the accumulated CO₂ in the test
3 chamber between measurements. The room air had between 300 and
4 700 ppm of CO₂ contamination. In subsequent tests using
5 nitrogen as the purge gas with negligible levels of CO₂
6 contamination, the same test could be completed within several
7 hours because of improved signal discrimination from the
8 background and when using linear regression for calculating the
9 slopes or accumulation rates.

10

11 In addition to whole packages (e.g. test samples 17, 18),
12 the technique could also be used to measure permeability of
13 bottles or closures alone. For testing bottles, a suitable
14 impervious liner could be used to seal the bottle. For
15 example, aluminum foil seal liners could be used. When
16 closures are of interest, an impervious bottle could be used in
17 conjunction with the closure of interest. For example,
18 stainless steel bottles with matching finish and the closure of
19 interest could be use as a test package sample. The apparatus
20 and technique could also be used when one is interested in
21 measuring CO₂ evolution (and thus respiration rates) of
22 biological samples and in testing materials that outgas
23 specific compounds that could be detected by the sensor 13.

1 In plastic packages, often the closure members are made
2 out of a different material (e.g. nylon or polypropylene caps
3 with polyethylene or aluminum liners) than the container (e.g.
4 polyethylene terephthalate or PET). Upon filling such packages
5 with a product, if they are exposed to changes in temperatures
6 (e.g., a bottle containing a beverage is chilled on ice), the
7 different materials expand or contract differently because of
8 differing thermal expansion coefficients, and could cause the
9 closure to back-off or the seal to separate from the bottle
10 finish affecting the gross package integrity. Accordingly,
11 there is a need for rapidly assessing package integrity under
12 conditions of temperature cycling. The current invention
13 readily allows testing for package integrity under temperature
14 cycling, i.e., varying temperature within chamber 10 during the
15 measuring procedure according to a predetermined program to
16 determine gross package integrity. For causing the package
17 temperatures to change rapidly, the preferred method is to fill
18 the bottles substantially fully with gaseous permeant (e.g. dry
19 ice). If moisture is required for sealing performance, a small
20 amount of water could be incorporated into the package. The
21 test chamber temperature is varied according to a predetermined
22 program and the sensor signal monitored continuously for sudden
23 changes in permeant accumulation. The performance of the
24 package seal is thus assessed under varying thermal loads.

1 The same methods can also be used to measure
2 permeabilities of packaging films as follows. Attention is now
3 drawn to FIG. 3, which is a simplified sectional view showing
4 the makings of such a test package, designated 45. In this
5 case, a test film 33 is mounted on a substantially impervious
6 attachment 27 using O-rings 28 and 29. A screen 30 on the
7 outside of test film 33 provides mechanical support and
8 protects test film 33 from rupturing due to pressure variations
9 thereacross. A retaining ring 31 fastens the film-screen
10 assembly to attachment 27 by threaded connection. Alternative
11 means of fastening the film-screen assembly to attachment 27,
12 or similar structure can be employed (for example, TriClampTM or
13 other suitable flange clamping mechanisms) without deviating
14 from the spirit of this invention. It is also possible to
15 plumb the test chamber with a permeant source and provide for a
16 mechanism of clamping the membrane directly to the inside of
17 the test chamber. Attachment 27 is connected by another
18 threaded connection or other suitable means to a container 32,
19 which is also made of suitable impervious materials such as
20 steel, aluminum, or glass.

21

22 Container 32 contains a substance including the permeant
23 or a substance that generates the permeant. Once one or more
24 packages 45, such as those of FIG.3, are assembled, a suitable
25 number of them could be used in place of packages or test

1 samples 17 and 18 of FIG.1 to conduct permeation tests. When
2 support screen 30 is employed, the measured permeation rate
3 needs to be multiplied with a correction factor to account for
4 the portion of the film area that is covered by the screen and
5 is not active in permeation. Alternatively, standard test
6 films whose permeability characteristics are known in advance
7 could be tested with the screen and the ratio of the measured
8 permeability to the known permeability could be used to
9 determine such screen correction factors. When the support
10 screen has a substantially open pore structure, the correction
11 factor could be altogether neglected.

12
13 Next we turn to the application of measuring the amount of
14 permeant adsorbed by the packaging materials. Following
15 equilibration, the package (e.g. package 45 or test samples 17,
16 18) is emptied of its contents and placed in chamber 10. An
17 accumulated permeant amount in the internal space of chamber 10
18 will directly correspond to the amount of permeate dissolved
19 into the packaging materials. Two types of data analyses is
20 possible. In Method 1, the package is left in chamber 10 for a
21 prolonged time until no further accumulation is detected.
22 Depending on the quantity of permeant absorbed, it may be
23 necessary to conduct one or more purge cycles if the
24 accumulating permeant concentration meets or exceeds the high
25 concentration limit of the sensor measurement range. The final

1 concentration level attained multiplied by the volume in
2 chamber 10 represents the amount of adsorbed permeant.

3

4 Results of an example of Method 1 testing are shown as a
5 plot in FIG. 6. In this test, a carbonated soft drink bottle
6 is emptied of its contents, rinsed with water to remove all
7 residual carbonated water, and placed in test chamber 10. The
8 chamber temperature is raised to 120°F to speed up the process
9 of desorption, and the concentration of the permeant (CO₂) is
10 continuously monitored. The amount of permeant desorbed at any
11 time is calculated as the product of the sensed concentration
12 and the test chamber volume, and is plotted in FIG. 6. The
13 symbols represent actual amounts calculated thus, and the solid
14 line is a simple exponential desorption model used to fit the
15 experimental data in order to calculate the final amount of
16 sorbed CO₂ in the package.

17

18 In data analysis Method 2, the time history of
19 concentration change can be reconciled with a mathematical
20 model of the transient permeant diffusion process. The
21 mathematical model consists of solving either analytically or
22 numerically the diffusion equation for permeate diffusion in
23 the packaging material. Permeant solubility or sorption and
24 diffusivity parameters that best describe the experimentally

1 observed transient permeation behavior are then estimated by
2 any suitable algorithm.

3

4 Method 2 is preferable when the total amount of adsorbed
5 permeant is small or when the packaging materials have good
6 permeant barrier properties (i.e., exhibits very poor diffusion
7 for the permeant). Under such conditions, equilibrium
8 desorption will take an inordinately long time requiring one to
9 measure small sensor signals against noise over very long
10 periods. In addition, even the tiniest leaks in the chamber
11 could produce significantly erroneous results as well as other
12 materials used in the chamber may begin to adsorb the permeant
13 appreciably and interfere with the test method.

14

15 A more sensitive method for measuring the solubility of
16 permeant in the packaging materials involves equilibrating open
17 packaging materials with the permeant under pressure in a
18 separate container, depressurizing and flushing the open
19 packages with an inert medium to rid them of all entrained
20 permeant, and then testing for sorption using the method above.
21 This approach enables loading the packaging materials with
22 significantly larger quantities of the permeant than is
23 possible by the conventional packaging approach because much
24 higher pressures can be used to drive sorption. Higher levels
25 of permeate sorption are easier to measure accurately and

1 therefore, this method improves sensitivity. Since permeation
2 occurs from both the inside and outside surfaces of the open
3 package, an analytical solution for the diffusion equation is
4 available without the need for complicated numerical algorithms
5 resulting in a very robust process for measuring sorption.

6
7 Next we turn to the preferred procedures for controlling
8 the test conditions (temperature and relative humidity) for
9 applications where such special controls are required. If the
10 test can be conducted in a controlled environment room, it is
11 unlikely that the following design modifications would be
12 needed except when sensor 13 produces enough heat to
13 appreciably change the temperature in test chamber 10.
14 Nevertheless, the following specifications describe a preferred
15 embodiment. Attention is drawn to FIG. 4 in which some
16 additional modifications to chamber 10 of FIG. 1 are shown in a
17 semi-schematic drawing. A temperature sensor 34 measures the
18 temperature in chamber 10. Ideally, this would be a resistance
19 thermometer or a thermistor, but thermocouples or any other
20 suitable elements could be employed. A heater and/or cooler
21 element 35 adds or removes heat from the chamber as required to
22 maintain the temperature sensed by temperature sensor 34 at the
23 desired set point temperature. The amount of heat added or
24 removed will be dependent on the deviation of the actual
25 temperature from the set point temperature and is determined by

1 any suitable algorithm that is implemented by a temperature
2 controller. The heater and cooler could be two separate
3 elements, but preferably are combined into a single element
4 such as a thermoelectric or Peltier device.

5
6 The humidity in chamber 10 could be controlled in one of
7 three ways. If the packages themselves do not transmit
8 significant amounts of water vapor from within, the inert
9 medium used to purge the chamber could be prehumidified to the
10 desired level. The simplest, and perhaps most accurate method
11 is to place a small container 36 in the chamber with a
12 saturated solution of any suitable substance in water in the
13 chamber. For example, moist sodium chloride (table salt) will
14 control the humidity at near 75% relative humidity. Other salt
15 solutions can be judiciously chosen and employed in a similar
16 manner to achieve the desired relative humidity. Other useful
17 examples are saturated magnesium nitrate solution controls
18 relative humidity at 54% at about 70°F, potassium nitrate
19 solution controls relative humidity at 95%, and lithium
20 chloride solution controls relative humidity at 11%.
21 Preferably, the material of construction for the salt solution
22 container, as well as the salt solution itself will consist of
23 inert formulations that do not absorb or emit the permeant
24 themselves. When the permeant of interest is CO₂, sorption of
25 CO₂ by the salt solution could be substantially eliminated by

1 decreasing the pH of the salt solution below approximately pH
2 4.5 by adding sufficient appropriate quantities of a suitable
3 acid. Even without such pH control steps, the concentration of
4 the permeant in the chamber is usually at least 1.5 to 2 orders
5 of magnitude lower than in the test packages. Thus the driving
6 force for sorption into the humidity control solution is not
7 likely to be significant compared to the quantities in the test
8 packages themselves.

9

10 One disadvantage with using open containers of salt
11 solutions is that as the water evaporates from the solution,
12 "salt fingers" form that eventually creep out of the container
13 into the outside space. The resulting salt deposits on the
14 equipment, while being a nuisance, can corrode equipment and
15 also interfere with other functions of the apparatus.
16 Moreover, the surface area for vapor exchange is limited to the
17 top liquid surface and thus somewhat reduces the efficiency of
18 humidity control, particularly in large volume chambers.

19

20 In a different embodiment, container 36 can be replaced,
21 supplemented, or filled with packages or small bags, designated
22 36A, of a saturated solution of any suitable substance. The
23 packages or bags 36A are formed of a suitable material that
24 allows interaction between the atmosphere within cavity 10 and
25 the saturated solution of a suitable substance contained in

1 bags or packages 36A. Preferably the interaction occurs
2 without allowing the saturated solution to flow out of the bags
3 or packages 36A into chamber 10. In a preferred embodiment
4 bags or packages 36A are formed of a hydrophobic microporous
5 material, made from polypropylene, polytetrafluoroethylene
6 (TeflonTM) or other suitable materials. Commercial materials
7 such as Celgard 2500TM or GORTEXTM, or even TyvekTM can be
8 employed. The pore structure of these materials is such that
9 while they allow for relatively free water vapor diffusion into
10 and out of the bags, the hydrophobic nature prevents the liquid
11 phase from passing through at normal operating pressures
12 relevant for the current application. Bags or packages 36A
13 could be pre-filled and designated with a specific
14 substantially constant humidity that can be achieved with that
15 specific bag or package, e.g. taking into account the size of
16 the bag and the amount and type of saturated salt solution
17 contained therein. By appropriate choice of the salt, bags or
18 packages 36A can be designed for very specific humidity,
19 additional measuring devices may not be required. In fact,
20 once such a humidity control method is incorporated, the test
21 chamber may be used to calibrate humidity sensors. Also, bags
22 or packages 36A can be easily introduced into chamber 10 and
23 removed without causing undue cleaning problems.

1 Alternatively, humidification can be accomplished by
2 ejecting droplets or a stream of water into chamber 10 with a
3 suitable volumetric addition device 37, for example, a
4 piezoelectric ejector. For this type of humidity control, a
5 humidity sensor 38 is also required for sensing the prevalent
6 humidity level relative to the desired set point. A controller
7 will then take into account the deviation in actual humidity
8 from the set point value and adjust the rate and amount of
9 water injection into chamber 10 based on a suitable algorithm.
10 Preferably, temperature sensor 34 and humidity sensor 38 are
11 combined into a single probe. When the test packages
12 themselves do not emit significant amounts of water vapor, it
13 is possible to conduct the permeation tests at near the desired
14 humidity levels if the inert gas medium used to flush the
15 chamber is pre-humidified appropriately.

16
17 Typical package permeation rates are slow enough that
18 molecular diffusion of the permeant is sufficient to
19 substantially eliminate permeant concentration gradients in
20 chamber 10. However, for packages that rapidly emit the
21 permeant, the concentration in chamber 10 may not be uniform,
22 and the concentration measured by sensor 13 would not truly
23 represent permeant concentration throughout the chamber space.
24 Under these conditions, it is desirable to agitate or stir the
25 medium in the chamber space to substantially eliminate

1 concentration gradients. A technique to achieve this is to
2 have a spring-loaded movable member 39 positioned in chamber 10
3 that could be coupled magnetically to an external drive
4 electromagnet 40. When electromagnet 40 is energized, movable
5 member 39 is drawn toward electromagnet 40 causing a large
6 movement of the medium in container 10, and when electromagnet
7 40 is de-energized, the tension in the spring returns movable
8 member 39 to its original position. Such convection inside
9 chamber 10 is sufficient to achieve good mixing.
10 Alternatively, a turbine or a fan could be readily incorporated
11 with due regard to their construction and material properties
12 so that the integrity of the test chamber is not compromised.

13
14 Thus, new and improved apparatus and techniques for
15 measuring package permeability have been disclosed. The new
16 and improved apparatus and techniques can be used for measuring
17 package permeability and/or measuring package permeant
18 sorption. The new and improved apparatus and techniques for
19 measuring package permeability and/or permeant sorption include
20 accurate control of humidity and temperature and new and
21 improved apparatus for more accurately controlling humidity.
22 Also, the new and improved package permeability measuring
23 apparatus and techniques are extremely accurate and
24 substantially faster than prior art apparatus and techniques.
25 Further, the new and improved package permeability measuring

1 apparatus and techniques can be used on substantially any
2 types, shapes, and sizes of packages.

3

4 Various changes and modifications to the embodiments
5 herein chosen for purposes of illustration will readily occur
6 to those skilled in the art. To the extent that such
7 modifications and variations do not depart from the spirit of
8 the invention, they are intended to be included within the
9 scope thereof which is assessed only by a fair interpretation
10 of the following claims.

11

12 Having fully described the invention in such clear and
13 concise terms as to enable those skilled in the art to
14 understand and practice the same, the invention claimed is: